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Effect of humidity on ammonia sensing by molecular materials

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Abstract:

In gas sensor domain, cross-sensitivity between humidity and ammonia is not well studied in literature. Humidity can induce variation on gas sensor responses and also affect the devices lifespan. The aim of the present work is to clarify the effect of humidity on the response of a resistor used for NH_3 monitoring in air quality applications. This survey performs experiments under different relative humidity levels to verify the effect of humidity on the conductivity of the sensing element. Then, the sensor was exposed to different humidity levels and NH_3 concentrations to statute on cross-sensitivity of sensors. The device made from a molecular material exhibits a response stable to ammonia in the range of 20-60% of relative humidity.

Keywords: Gas sensor, ammonia, humidity, molecular material, cobalt phthalocyanine.

Introduction

Ammonia is a well spread chemical product used as a raw material for producing fertilizers and also as a refrigerant in food industry [1,2]. The profusion of this gas induced a safety risk over industrial employees due to its toxicity. That is why exposure limit was set. In Europe, the air quality labour legislation sets a daily exposure limit at 20 ppm. This limitation created a need for monitoring NH_3 concentrations in air as a safety measure. Many detectors are available for sale and cover this range. However, within an industrial environment the effect of humidity is not very well known. Moreover, a cost effective and simple sensor could interest industrials. That is why we did conduct a survey of combined NH_3 and humidity effects, with cobalt phthalocyanine (CoPc) as sensitive molecular material. Phthalocyanines are well known as semiconductor [3,4] and their uses in gas sensors [5-7] particularly in air quality control [8-10]. Our lab did conduct a previous survey on NH_3 and CoPc diluted in dry Ar [11]. This work and another one on the effect of NH_3 and wet atmospheres on the conducting properties of lutetium bisphthalocyanine thin films [12] were used as a starting point to developed an NH_3 workbench and allow this study for measuring conductivity of sensing layer exposed to different NH_3 concentrations and relative humidity (RH) levels.

Experimental

The sensing element (CoPc) was deposited onto Interdigitated electrodes (IDEs) made of Indium Tin Oxide (ITO) deposited on a floated glass substrate. The product was evaporated (using a VEECO 770 system) at *ca.* 10^{-6} mbar and at a 2 $Å.s^{-1}$ rate. The thickness (100 nm) was controlled by means of a quartz microbalance.

The ammonia workbench performs conductivity measurements and control three 5850S Brooks mass flow controllers (MFCs) that regulate the flow rates of gases. All experiments were carried out in ambient conditions (temperature and pressure). In Fig. 1 are represented two MFCs that control a main stream of 500 $mL.min^{-1}$. This main line supply the measurement cell, a cylindrical Teflon chamber (*ca.* 10 cm^3 internal volume), with an Ar flow charged with humidity. The RH was controlled through the balance of MFCs and monitored by a Vaisala HMT100 humidity sensor. Then, NH_3 concentration in the chamber controlled by a third MFC via a secondary line used for the injection of a NH_3 flow. Finally, the sensor is alternately exposed to exposure/recovery cycles (1 and 4 minutes, respectively) while regulating humidity levels. The switching between exposure and recovery is a dynamic exposure setting, a method that allows an estimation of concentrations with the help of relative response (RR) calculation (eq. (1)).

$$\frac{\Delta\sigma}{\sigma_0} = \frac{\sigma_f - \sigma_0}{\sigma_0} \quad (1)$$

where σ_0 is the conductivity value at the beginning of an exposure/recovery cycle and σ_f the conductivity value at the end of the same cycle. The conductivity and relative response (RR) were plotted *versus* time to depict the effect of humidity on the response to ammonia.

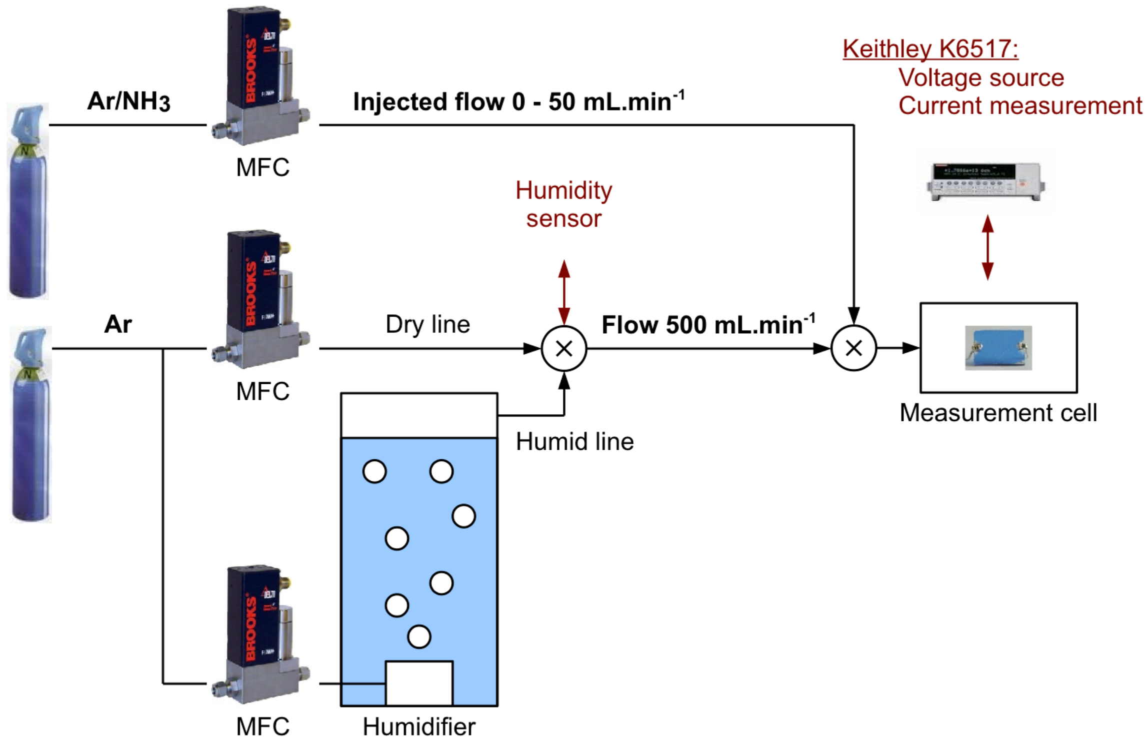

Fig. 1. Ammonia workbench with controlled humidity.

Results

Before testing the effect of humidity on the sensor conductivity, CoPc film was exposed to high RH atmospheres. The CoPc is not soluble in water and, as expected, the sensing layer remained unimpaired. No sign of alteration was observed in the 0-80% RH range as well in further experiments under NH_3 and humidity. A different RH level was set by step of 10% in the 0-80% range. Each step was maintained during 15 minutes and then changed. Then, the conductivity was plotted as a function of time (see Fig. 2). The result of conductivity experiment exposed to different humidity levels showed that the variation at the switching moment between two humidity levels was small. However, when the RH dropped below 20% the increase in conductivity became quite large, especially from 20 to 10%. A sharp increase could also be observed when lowering the humidity level from 10% to 0% RH. This dramatic effect can be attributed to the drying of material. Thus it is possible to conclude that CoPc conductivity increases at very low RH levels.

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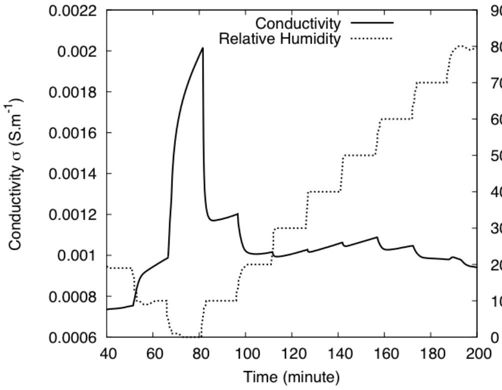

Fig. 2. Conductivity (solid line) as a function of time of a CoPc resistor exposed to different humidity levels (dotted line).

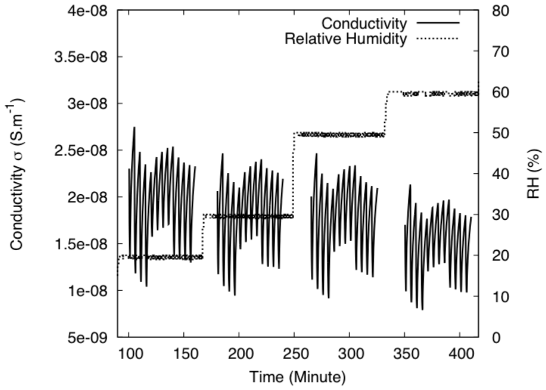

Fig. 3. Conductivity (solid line) as a function of time of a CoPc resistor exposed to NH_3 diluted in Ar at different concentrations for 1 min-long periods spaced by a 4 min-long static rest period. This measurement was realized for 4 different humidity levels (dotted line) 20, 30, 40 and 60% RH, respectively and for 4 exposure/recovery cycles at 3 different supplementary flow of 50, 25 and 12.5 mL.min^{-1}, (87, 45 and 23 ppm NH_3).

The next test for this study was the mixing of humidity and NH_3. CoPc resistor was exposed to NH_3 at different concentrations, successively 87, 23 and 45 ppm. Each exposure of 1 min-long was followed by a 4 min-long rest period. These exposure/recovery cycles were repeated four times. At each NH_3 concentration this measurement was realized for 4 different humidity levels (dotted line), namely 20, 30, 40 and 60% RH, respectively. In Fig. 3 are plotted as functions of time the conductivity and the RH. The conductivity is only plotted during the exposure/recovery cycles. As studied previously [11], the conductivity of CoPc decreases during exposure to NH_3 and then increases during recovery period. For the same RH it can be possible to clearly observed the four exposure/recovery cycles at each NH_3 concentrations. The variations of humidity levels for the same set of concentrations keep the relative response of the conductivity stable. From Fig. 3, we can conclude that the response of CoPc to NH_3 is stable at any RH value, in the range 20-60%, the conductivity variation depends solely on the NH_3 concentration.

In order to clarify the unsensitivity of the response to the effect of the relative humidity, another experiment was conduct for two levels of humidity, 30 and 40% RH levels, where 10 NH_3 concentrations were used, namely 2, 9, 19, 28, 37, 45, 54, 62, 71, 79, and 87 ppm. Those parameters were chosen due to their proximity with ambient humidity during a year. A calibration curve of the relative response as a function of NH_3 concentration was plotted (see Fig. 4).

The two curves were almost joining themselves and allow us to conclude that humidity has only small effect on the response to NH_3.

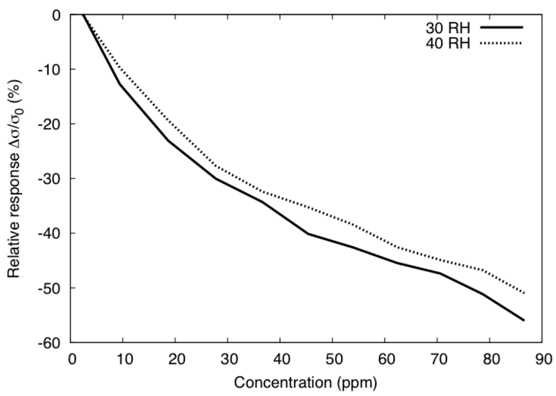

Fig. 4. Relative response as a function of the NH_3 concentration of a CoPc resistor at 30% (solid line) and 40% (dotted line) RH levels.

Conclusion

CoPc exhibits a response mainly unsensitive to humidity above 20%RH. Moreover this survey conducted in the 0-87 ppm range demonstrates that the detection limit set by the European community is reachable. Furthermore, CoPc as a sensor got an easy processability, which does not require either a heating set up or a complementary humidity sensor. This study of the effect of humidity on NH_3 sensor response allows us to conclude that CoPc is a good material for air quality monitoring applications in ambient conditions.

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References

[1] B. Timmer, W. Olthuis, A. van den Berg, Ammonia sensors and their applications—a review, *Sensors and Actuators B* 107, 666-677 (2005); doi: 10.1016/j.snb.2004.11.054

[2] M. Bouvet, A. Pauly, Molecular Semiconductor - Based Gas Sensors in: The Encyclopedia of Sensor, C.A. Crimes, E.C. Dickey, M. Pishko (Eds.), American Scientific Publishers, 227-270 (2006). ISBN: 1-58883-056-X/$50.00

[3] G. Guillaud, M. Al Sadoun, M. Maitrot, J. Simon, M. Bouvet, Field-effect transistor based on intrinsic molecular semiconductors, *Chemical Physics Letters* 167, 503-506 (1990); doi: 10.1016/0009-2614(90)85459-P

[4] M. Bouvet, J. Simon, Electrical properties of rare earth bisphthalocyanines and bisnaphthalocyanines complexes, *Chemical Physics Letters* 172, 299-302 (1990). Doi : 10.1016/0009-2614(90)85407-4

[5] G. Guillaud, J. Simon, J.P. Germain, Metallophthalocyanines: Gas sensors, resistors and field effect transistors, *Coordination Chemistry Reviews* 178–180, 1433-1484 (1998); doi: 10.1016/S0010-8545(98)00177-5

[6] J.D. Wright, Gas adsorption on phthalocyanines and its effects on electrical properties, *Progress in Surface Science* 31, 1-60 (1989). doi : 10.1016/0079-6816(89)90012-9

[7] F.I. Bohrer, A. Sharoni, C.N. Colesniuc, J. Park, I.K. Schuller, A.C. Kummel, W.C. Trogler, Gas Sensing Mechanism in Chemiresistive Cobalt and Metal-Free Phthalocyanine Thin Films, *Journal of the American Chemical Society* 129, 5640-5646 (2007). doi: 10.1021/ja0689379

[8] J. Brunet, A. Pauly, C. Varenne, B. Lauron, On-board phthalocyanine gas sensor microsystem dedicated to the monitoring of oxidizing gases level in passenger compartments, *Sensors and Actuators B* 130, 908-916 (2008); doi: 10.1016/j.snb.2007.10.074

[9] M. Bouvet, A. Leroy, J. Simon, F. Tournilhac, G. Guillaud, P. Lessnick, A. Maillard, S. Spirkovitch, M. Debliquy, A. de Haan, A. Decroly, Detection and titration of ozone using metallophthalo-cyanine-based field-effect transistor, *Sensors and Actuators B* 72, 86-93 (2001). doi: 10.1016/S0925-4005(00)00630-4

[10] M. Bouvet, G. Guillaud, A. Leroy, A. Maillard, S. Spirkovitch, F.-G. Tournilhac, Phthalocyanine-based field-effect transistor as ozone sensor *Sensors and Actuators B*, 73, 63-70 (2001). doi: 10.1016/S0925-4005(00)00682-1

[11] T. Sizun, M. Bouvet, Y. Chen, J.-M. Suisse, G. Barochi, J. Rossignol, Differential study of substituted and unsubstituted cobalt phthalocyanines for gas sensor applications, *Sensors and Actuators B* 159, 163-170 (2011). doi: 10.1016/j.snb.2011.06.067

[12] V. Parra, M. Bouvet, J. Brunet, M.-L. Rodríguez-Méndez, J.A. de Saja, On the effect of ammonia and wet atmospheres on the conducting properties of different lutetium *bis*phthalocyanine thin films, *Thin Solid Films* 516, 9012-9019 (2008); doi: 10.1016/j.tsf.2007.11.092